

## **FINAL REPORT OF AOARD-64-044 CONTRACT**

### **High Efficiency and Long Life Hybrid Photovoltaic Research for Space Applications**

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#### **Abstract**

We have developed a tree-like nanostructured photovoltaic device based on the polymer poly(3-hexylthiophene)(P3HT)/metal oxide hybrid materials by solution processes at low temperature. An array of large ZnO nanorods with a larger size of 50 nm in diameter and 150 nm in length are grown to act as tree trunks for efficient charge collection. Small TiO<sub>2</sub> nanorods with a size of 5 nm in diameter and 20 nm in length are incorporated to act as tree branches for facilitating charge separation and transport. The device based on the tree-like nanostructure exhibits a short circuit current density  $>2 \text{ mA/cm}^2$  under A.M. 1.5 illumination, showing over seven times increase compared to that without the incorporation of TiO<sub>2</sub> nanorods. Efficient charge separation and transport in the tree-like nanostructured photovoltaic device has further been demonstrated by time-resolved photoluminescence spectroscopy and transient photocurrent measurements.

#### **Introduction**

Recently, composites of organic polymers and inorganic nanocrystals have attracted a great of interest due to their potential application in developing the low-cost, large-area, mechanically flexible photovoltaic devices<sup>1,2</sup>. A basic requirement for a photovoltaic material is to generate free charge carriers produced by photoexcitation. Subsequently, these carriers are transported through the device to the electrodes without recombining with oppositely charged carriers. Due to the low dielectric constant of organic materials, the dominant photogenerated species in most conjugated polymer is a neutral bound electron-hole pair (exciton). These neutral excitons can be dissociated from Coulomb attraction by offering an energetically favorable pathway for the electron from polymer (donor) to transfer onto an electron-accepting specie (acceptor). Because the diffusion length of excitons in a semiconducting polymer is usually shorter than  $20 \text{ nm}^{3-5}$ , the electron acceptor must be intermixed with polymer at a nanometer length scale to achieve efficient charge separation. The most commonly

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used structure is the polymer-based bulk heterojunction (BHJ) solar cell, which consists of the electron accepting network formed randomly within the polymer matrix. The most popular electron acceptors in the BHJ polymer photovoltaic devices are C<sub>60</sub> derivatives<sup>6,7</sup> and nanocrystals such as CdSe<sup>1,8</sup> or TiO<sub>2</sub><sup>9-11</sup>. After charge separation, electrons and holes must be transported to the opposite electrode before back recombination occurs. Carrier transport in the BHJ photovoltaic devices is usually limited by the poorly formed electron conducting pathway through hopping. A promising photovoltaic device structure consisting of a direct and ordered path for photogenerated electrons to the collecting electrode has been proposed<sup>12</sup>. This can be done by using templated porous nanostructures<sup>13-15</sup>, or vertically oriented nanorods<sup>16-18</sup>. ZnO nanorods grown perpendicularly to the substrate have attracted a great interest recently since they can be synthesized through simple processes from solution at low temperature. The photovoltaic devices based on the conjugated polymer deposited onto ZnO nanorods<sup>17</sup> or nanofibers<sup>18</sup> have been demonstrated recently. Although the optimized structural dimension of less than 20 nm between nanorods is desirable, it is still very challenging in controlling the precise spacing between nanorods for infiltrating polymer. In Ref.17, an amphiphilic molecular dye interface between ZnO nanorods and polymer is therefore required to assist charge separation due to the large film pore sizes (~100 nm) between nanorods. In this article, we propose a tree-like nanostructured photovoltaic device based on the ZnO/P3HT:TiO<sub>2</sub> hybrid material as shown in Figure 1 schematically. Thicker ZnO nanorod arrays are grown on the electrode surface to act as the tree trunks for efficient electron collection. The thinner TiO<sub>2</sub> nanorods are then incorporated to act as the tree branches to provide large interfacial areas and direct pathways for assisting charge separation and transport respectively. Considerable improvement over seven times greater in the shorts circuit current (>2 mA/cm<sup>2</sup>) can be achieved in the tree-like nanostructured photovoltaic device by infiltrating the P3HT:TiO<sub>2</sub> hybrid material with respect to that by infiltrating the polymer only.

ZnO nanorod arrays were grown on Au-coated ITO substrates using pulsed current electrolysis method. Au layers with a thickness of ~ 10nm were pre-deposited on the ITO substrates using DC sputtering. The substrate, a platinum wire and an Ag/AgCl electrode were utilized as the working, the counter and the reference electrodes, respectively, in an electrochemical system. A 0.0025M aqueous solution of Zn (NO<sub>3</sub>)<sub>2</sub> was employed to be the electrolyte. A pulsed wave with a pulse length and a pulse period of 0.01 and 0.1s, respectively, were used for the growth of ZnO nanorods. The pulsed current density was -2 mA/cm<sup>2</sup>. Figure 2(a) shows the typical scanning electron micrograph (SEM) of the ZnO nanorod array formed using pulsed current electrolysis method at 80 °C. The diameter and the length of the ZnO

nanorods are about 50 nm and 150 nm, respectively. The average spacing between nanorods is of the order of ~120 nm. High aspect ratio anatase TiO<sub>2</sub> nanorods were synthesized by the hydrolysis of titanium tetraisopropoxide as described previously<sup>19</sup>. The high-resolution transmission electron microscopy (HRTEM) image of TiO<sub>2</sub> nanorods in Figure 2(b) reveals that the dimension of TiO<sub>2</sub> nanorods is about 5 nm in diameter and 20 nm in length. In the preparation of hybrid materials, the P3HT solution was prepared by dissolving P3HT (Aldrich, USA) in chloroform. The solutions of hybrid materials with 50wt% TiO<sub>2</sub> nanorods were obtained by mixing the required amount of TiO<sub>2</sub> nanorods solution with the P3HT solution. For the photovoltaic device fabrication, a thin active layer is deposited onto ZnO nanorods by using spin coating. The thin active layer was used as hole transporting and light absorbing material. The device was then fabricated by spin-coating a layer of PEDOT:PSS with an effective thickness of 50 nm before thermal evaporation of the Au top electrode. The highly conductive PEDOT:PSS layer is intended to keep the serial resistance low and to reduce surface roughness by filling the voids in the films. All the above device fabrication processes were performed in air. The films were then baked in a vacuum oven for 6 hr at 120°C. Vapor deposition of the Au electrode was then carried out at pressure around 2x10<sup>-6</sup> Torr. For sample characterizations, time-resolved photoluminescence spectroscopy was performed with a time-correlated single photon counting (TCSPC) spectrometer (Picoquant, Inc.). A pulse laser (375 nm) with an average power of 1 mW operating at 40 MHz with a duration of 70 ps was used for excitation. Current-voltage measurements were obtained by using a solar simulator (Oriel Inc.) with the A.M.1.5 filter. Transient photocurrent measurements were performed by a frequency-tripled Nd:YAG pulsed laser ( $\lambda = 355\text{nm}$  and pulse width ~5 ns) and the signals were recorded by a digital oscilloscope (Tetronix TDS5052B). The film thickness was measured by means of the Veeco M6 surface profiler.

Charge separation efficiency at polymer/inorganic nanocrystal interfaces can be usually revealed through quenching of the photoluminescence (PL) efficiency and shortening of measured PL lifetime in polymer<sup>8,20</sup>. Four samples consisting of different configurations are taken for investigation. Sample A (P3HT) represents the pristine P3HT thin film deposited on the silicon substrate. Sample B (ZnO/P3HT) and Sample C (ZnO/P3HT:TiO<sub>2</sub>) represent the composites by spin coating neat P3HT and P3HT:TiO<sub>2</sub> nanorods hybrid thin active layers onto the array of ZnO nanorods respectively. The Sample D (ZnO/TiO<sub>2</sub>/P3HT:TiO<sub>2</sub>) has a similar configuration to the Sample C but is precoated with a very thin TiO<sub>2</sub> nanorods layer onto ZnO nanorods before the P3HT:TiO<sub>2</sub> nanorods hybrid layer is deposited. All these samples have a similar thickness about 200 nm. Figure 3 shows the PL decay spectroscopy for these

different samples. It is found that the PL lifetime  $\tau_B$  (643 ps) for the Sample B is shorter than that of the pristine P3HT thin film  $\tau_A$  (735 ps), indicating that charge separation occurs at the interfaces between P3HT and ZnO nanorods by providing a new non-radiative process for photogenerated excitons. As TiO<sub>2</sub> nanorods are blended with P3HT, a large number interfaces between polymer and TiO<sub>2</sub> nanorods are generated, leading to more efficient charge separation as a result of the shorter PL lifetime  $\tau_C$  (509 ps) for the Sample C compared to  $\tau_B$ . For the Sample D, the PL decay lifetime  $\tau_D$  (361 ps) is even shorter than  $\tau_C$  due to the increasing number of interfaces on the surface of ZnO nanorods by coating a thin TiO<sub>2</sub> nanorods layer before infiltrating the active layer. As a result, more efficient exciton dissociation occurs. The role of the thin TiO<sub>2</sub> nanorods layer can be as follow. Firstly, inserting this layer can create a second interfacial area for exciton dissociation that might increase the charge transfer rate. Secondly, the thin TiO<sub>2</sub> nanorods are able to be connected to the TiO<sub>2</sub> nanorods in the active P3HT:TiO<sub>2</sub> hybrid to form a continuous pathway for electron transport after charge separation. In the previous reports<sup>14,15</sup>, an additional titanium oxide thin film can also be used as a hole-blocking layer to prevent the direct contact between polymer and the ITO electrode.

The photovoltaic performance of the tree-like nanostructured device based on the ZnO/TiO<sub>2</sub>/P3HT:TiO<sub>2</sub> material is then characterized under simulated AM 1.5 illumination as shown in Figure 4(a). For comparison, the device based on neat P3HT film deposited onto ZnO nanorods is also shown. The device based on the ZnO/P3HT material exhibits a short circuit current density ( $J_{sc}$ ) of 0.3 mA/cm<sup>2</sup>, an open circuit voltage ( $V_{oc}$ ) of 335 mV, a fill factor (FF) of 0.40, and a power conversion efficiency ( $\eta$ ) of 0.04 %. The  $\eta$  of the device with a neat P3HT film deposited onto ZnO nanorods is higher compared to that in Ref.17 with a similar configuration, but is lower compared to that in Ref.18. One possible reason for the higher efficiency in Ref.18 may be due to the usage of a smaller diameter of ZnO nanofibers. The performance of the tree-like nanostructured device (ZnO/TiO<sub>2</sub>/P3HT:TiO<sub>2</sub>) exhibits the values for  $J_{sc}$ ,  $V_{oc}$ , FF, and  $\eta$  of 2.2 mA/cm<sup>2</sup>, 400 mV, 0.35, and 0.31% respectively. Over seven times increase in  $J_{sc}$  is achieved. The corresponding external quantum efficiencies (EQE) for the samples are also presented in Figure 4(b). The maximum EQE for the tree-like nanostructured solar cell is about 23% at 510 nm. Enhancement in the device performance based on the tree-like structure is mainly attributed to efficient charge separation from the increased interfacial area and to effective carrier transport from the formation of continuous pathways by incorporating TiO<sub>2</sub> nanorods. We have further characterized the transport properties of the photovoltaic devices through transient photocurrent measurements. Figure 5 shows the photocurrent decay curves of the above devices. It is found that the tree-like nanostructured device has a faster

responding time ( $\sim 0.5 \mu\text{s}$ ) with respect to the device consisting of a neat P3HT film onto ZnO nanorods ( $\sim 2.4 \mu\text{s}$ ), indicating that effective carrier transport can also be achieved through this design of the tree-like device architecture.

## **Conclusions**

We have developed a type of tree-like polymer/inorganic metal oxide hybrid photovoltaic device. Thicker nanorstructured ZnO nanorods are grown on the electrode surface to act as tree trunks for efficient charge collection. Thinner  $\text{TiO}_2$  nanorods are incorporated into the ZnO nanorods array to act as tree branches for facilitating charge separation and transport, by providing increased interfacial area and effective transport pathway. The performance of the photovoltaic device based on the tree-like structure improves by more than a factor of seven after the incorporation of  $\text{TiO}_2$  nanorods. Further optimizations in the dimension of ZnO and  $\text{TiO}_2$  nanorods, active layer film thickness and fabrication in inert atmosphere instead of ambient etc. are required for the improvement of device performance.

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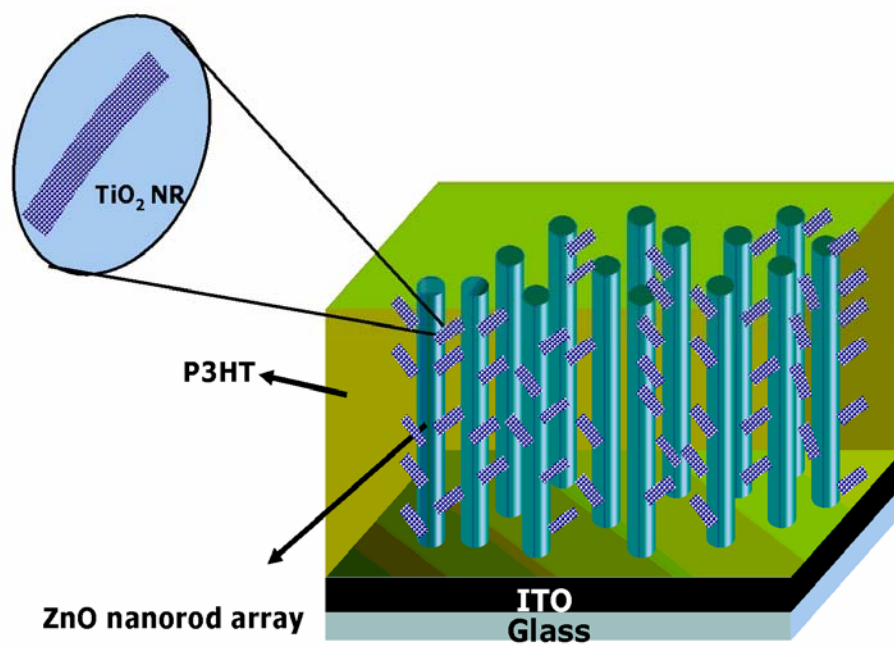
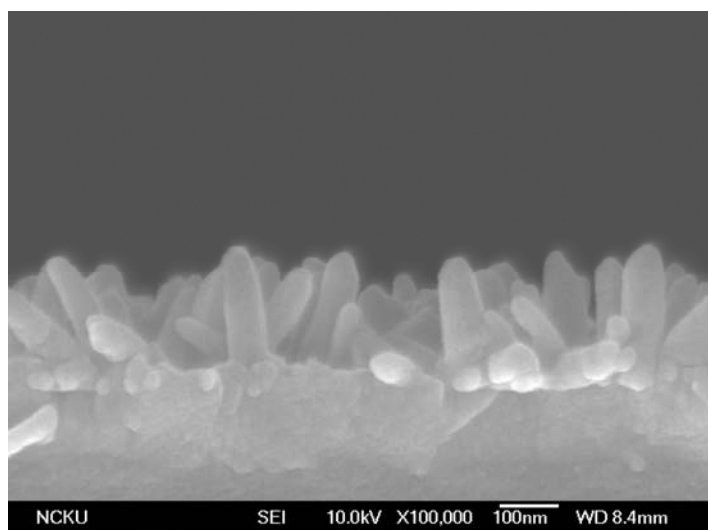


Fig.1 Schematic representation of the tree-like nanostructured photovoltaic device. Thicker ZnO nanorods act as tree trunks and thinner TiO<sub>2</sub> nanorods act as tree branches.





(b)

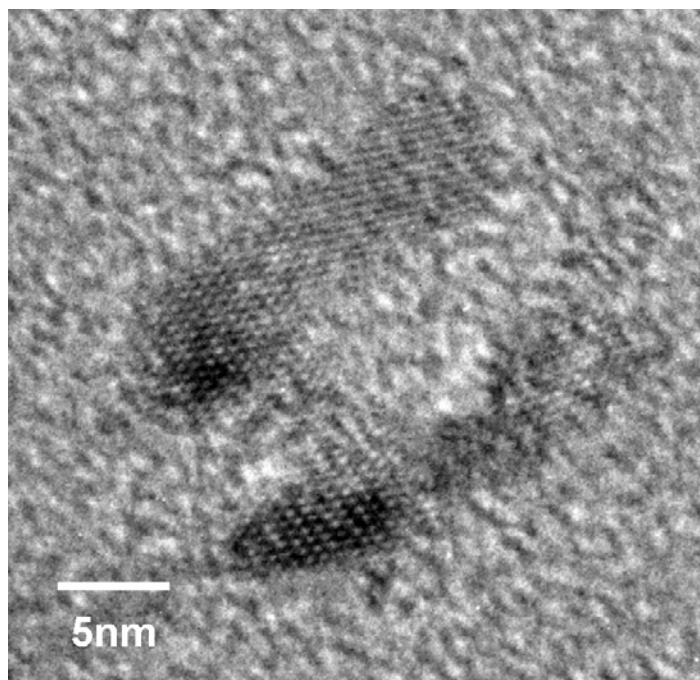


Fig.2 (a) Cross-sectional SEM micrograph of ZnO nanorod arrays. (b) High-resolution transmission electron microscopy (HRTEM) image of TiO<sub>2</sub> nanorods.

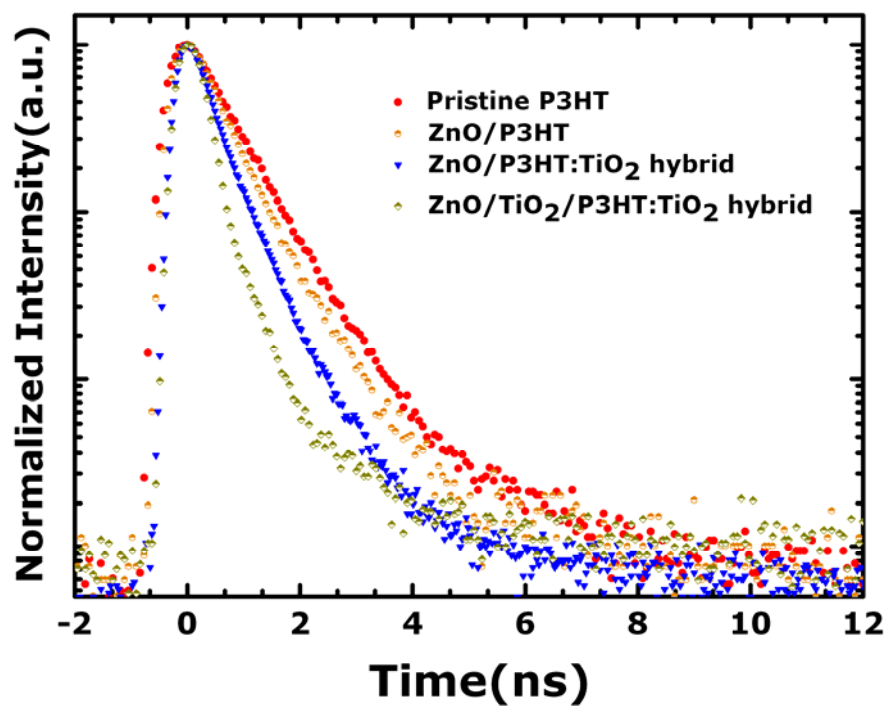
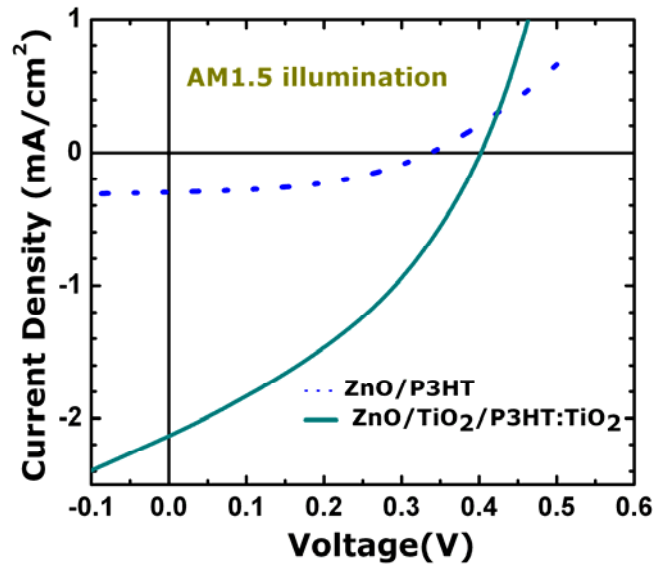


Fig.3 Time-resolved photoluminescence spectroscopy for the samples consisting of pristine P3HT(Sample A), ZnO nanorods/P3HT (Sample B), ZnO nanorods/P3HT:TiO<sub>2</sub> nanorods hybrid (Sample C) and ZnO nanorods/TiO<sub>2</sub> nanorods/P3HT:TiO<sub>2</sub> nanorods hybrid (Sample D) respectively.

(a)



(b)

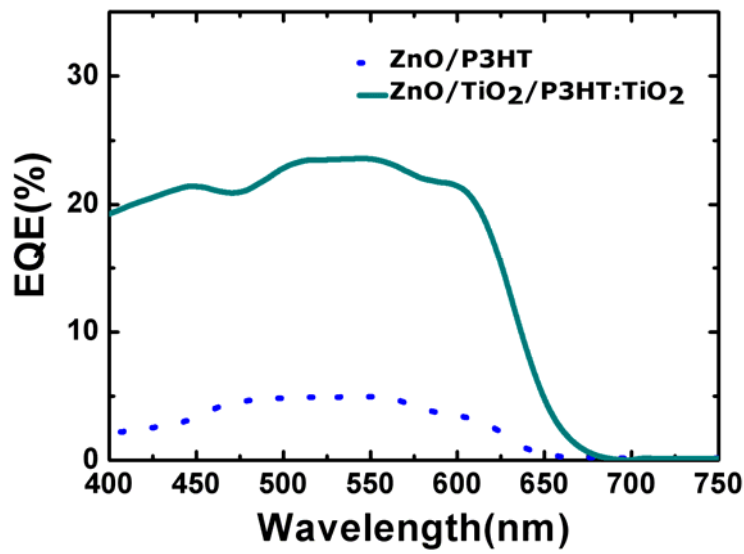


Fig.4 (a) Photovoltaic performances of the devices based on the ZnO/P3HT and ZnO/TiO<sub>2</sub> nanorods /P3HT:TiO<sub>2</sub> nanorods hybrid under simulated AM 1.5 illumination (100 mW/cm<sup>2</sup>). (b) External quantum efficiency (EQE) as a function of wavelength.

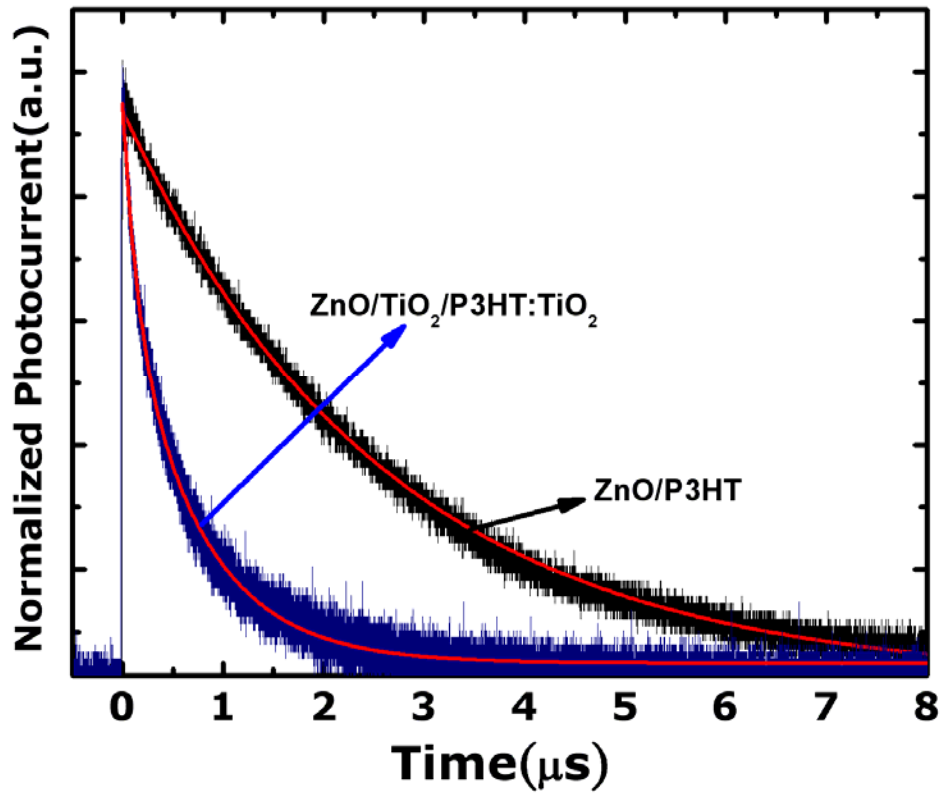


Fig.5. Transient photocurrent of the devices consisting of ZnO/P3HT and ZnO/TiO<sub>2</sub> nanorods/P3HT:TiO<sub>2</sub> nanorods hybrid thin active layers respectively.